G-33-470 #5

Final Report for Period: 05/2006 - 04/2007
Submitted on: 06/15/2007
Principal Investigator: Sherrill, Charles D.
Award ID: 0094088
Organization: GA Tech Res Corp - GIT
Title:
CAREER: Theoretical Studies of Bond-Breaking, Diradicals, and Nondynamical Correlation

Project Participants

Senior Personnel

Name: Sherrill, Charles
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Name: Hyde, Gerry
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Dutta, Antara
Worked for more than 160 Hours: Yes
Contribution to Project:
Dr. Dutta has obtained full CI potential energy curves for several small molecules and used them to assess various approximate correlation methods.

Graduate Student

Name: Sinnokrot, Mutasem
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Abrams, Micah
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Temelso, Berhane
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Bochevarov, Arteum
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Sears, John
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Ringer, Ashley
Worked for more than 160 Hours: Yes
Contribution to Project:

Supported by NSF Graduate Fellowship

Name: Yin, Fuchang
Worked for more than 160 Hours: No
Contribution to Project:

Name: Tauer, Tony
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Arnstein, Stephen
Worked for more than 160 Hours: Yes
Contribution to Project:

Undergraduate Student

Name: Park, Alfred
Worked for more than 160 Hours: Yes
Contribution to Project:

Technician, Programmer

Other Participant

Name: Derrick, Elizabeth
Worked for more than 160 Hours: Yes
Contribution to Project:

Research Experience for Undergraduates

Name: Steele, Ryan
Worked for more than 160 Hours: Yes
Contribution to Project:
Cation-pi modeling.

Years of schooling completed: Junior
Home Institution: Other than Research Site
Home Institution if Other: Iowa State
Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree
Fiscal year(s) REU Participant supported: 2002
REU Funding: REU site award

Name: Heldenbrand, Hugh
Worked for more than 160 Hours: Yes
Contribution to Project:

Years of schooling completed: Sophomore
Home Institution: Other than Research Site
Home Institution if Other: North Carolina State University
Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree
Fiscal year(s) REU Participant supported: 2003

REU Funding: REU site award

Name: Figgs, Michelle

Worked for more than 160 Hours: Yes

Contribution to Project:

Years of schooling completed: Junior

Home Institution: Other than Research Site

Home Institution if Other: University of Maryland, Baltimore County

Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree

Fiscal year(s) REU Participant supported: 2004

REU Funding: REU site award

Name: Takatani, Tait

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate worked on computing potential energy curves for multiple states of the NO molecule.

Years of schooling completed: Junior

Home Institution: Other than Research Site

Home Institution if Other: Marist College

Home Institution Highest Degree Granted(in fields supported by NSF): Bachelor's Degree

Fiscal year(s) REU Participant supported: 2005

REU Funding: REU supplement

Organizational Partners

IBM

IBM has supported this and other projects of ours by a large SUR grant of computer hardware. This has allowed us to establish a Center for Computational Molecular Science and Technology at Georgia Tech to support scientific computation.

Other Collaborators or Contacts

Our project is supported by the facilities and personnel of the Center for Computational Molecular Science and Technology (CCMST) at Georgia Tech. CCMST research scientist Dr. Edward Valeev (now Assistant Professor at Virginia Tech) contributed to this project both scientifically and as a system administrator of the CCMST supercomputer. We have engaged in informal collaborations with Prof. Alex MacKerell (University of Maryland), Prof. Ian Gould (Imperial College, London), Prof. Ursula Roethlisberger (Lausanne), Prof. Georg Jansen (Essen), among others, to provide high-quality ab initio data on noncovalent interactions to assist their efforts to develop force-field or improved DFT models for biomolecular simulations.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

See attached file

Findings: (See PDF version submitted by PI at the end of the report)

See attached file

Training and Development:

This project has provided nine graduate students and two postdocs with in-depth experience in the application of electronic structure methods to challenging systems. All have used a wide variety of program packages and have performed complex data analysis. Students Micah Abrams, Arteum Bochevarov, and John Sears have gained experience in the development of new theoretical methods by derivation, programming, and

benchmarking. An undergraduate gained experience in system administration in scientific computing environments (AIX and Linux operating systems), developed web pages, and wrote Perl programs to analyze data. Four undergraduate NSF REU students attended our introductory summer lectures in theoretical chemistry and learned to use quantum chemistry software to perform computations on noncovalent interactions.

Outreach Activities:

Some results of this study have been presented at several small colleges where students have frequently not had much exposure to current chemical research and do not generally plan on attending graduate school. These schools include: University of Tennessee, Chattanooga; Kilgore College, Texas; Panola College, Texas (nursing students); Old Dominion University; Hampton University (HBCU). These students frequently comment that they had no idea computers could be so helpful in understanding chemistry. It is hoped that they will better appreciate chemical research and that some of them will consider graduate school.

Journal Publications

Ryan D. Cohen and C. David Sherrill, "The Performance of Density Functional Theory for Equilibrium Molecular Properties of Symmetry Breaking Molecules", J. Chem. Phys., p. 8257, vol. 114, (2001). Published

Mutasem Omar Sinnokrot and C. David Sherrill, "Density Functional Theory Predictions of Anharmonicity and Spectroscopic Constants for Diatomic Molecules", J. Chem. Phys., p. 2439, vol. 115, (2001). Published

Anna I. Krylov and C. David Sherrill, "Perturbative Corrections to the Equation-of-Motion Spin-Flip SCF Model: Application to Bond-Breaking and Equilibrium Properties of Diradicals", J. Chem. Phys., p. 3194, vol. 116, (2002). Published

Micah L. Abrams, Edward F. Valeev, C. David Sherrill, and T. Daniel Crawford, "The Equilibrium Geometry, Harmonic Vibrational Frequencies, and Estimated Ab Initio Limit for the Barrier to Planarity of the Ethylene Radical Cation", J. Phys. Chem. A, p. 2671, vol. 106, (2002). Published

Mutasem Omar Sinnokrot, Edward F. Valeev, and C. David Sherrill, "Estimates of the Ab Initio Limit for Pi-Pi Interactions in the Benzene Dimer", J. Am. Chem. Soc., p. 10887, vol. 124, (2002). Published

Micah L. Abrams and C. David Sherrill, "A comparison of polarized double-zeta basis sets and natural orbitals for full configuration interaction benchmarks", J. Chem. Phys., p. 1604, vol. 118, (2003). Published

Antara Dutta and C. David Sherrill, "Full configuration interaction potential energy curves for breaking bonds to hydrogen: An assessment of single-reference correlation methods", J. Chem. Phys., p. 1610, vol. 118, (2003). Published

Edward F. Valeev and C. David Sherrill, "The diagonal Born-Oppenheimer correction beyond the Hartree-Fock approximation", J. Chem. Phys., p. 3921, vol. 118, (2003). Published

Edward F. Valeev, Wesley D. Allen, Rigoberto Hernandez, C. David Sherrill, and Henry F. Schaefer, "On the accuracy limits of orbital expansion methods: Explicit effects of k-functions on atomic and molecular energies", J. Chem. Phys., p. 8594, vol. 118, (2003). Published

John S. Sears, C. David Sherrill, and Anna I. Krylov, "A Spin-Complete Version of the Spin-Flip Approach to Bond Breaking: What is the Impact of Obtaining Spin Eigenfunctions?", J. Chem. Phys., p. 9084, vol. 118, (2003). Published

Micah L. Abrams and C. David Sherrill, "An Assessment of the Accuracy of Multireference Configuration Interaction (MRCI) and Complete-Active-Space Second-Order Perturbation Theory (CASPT2) for Breaking Bonds to Hydrogen", J. Phys. Chem. A, p. 5611, vol. 107, (2003). Published

Mutasem Omar Sinnokrot and C. David Sherrill, "Unexpected Substituent Effects in Face-to-Face pi-Stacking", J. Phys. Chem. A, p. 8377, vol. 107, (2003). Published

Artcum D. Bochevarov, Edward F. Valeev, and C. David Sherrill, "The Electron and Nuclear Orbitals Model: Current Challenges and Future Prospects", Mol. Phys., p. 111, vol. 102, (2004). Published

Berhane Temelso, Edward F. Valeev, and C. David Sherrill, "A Comparison of One-Particle Basis Set Completeness, Higher-Order Electron Correlation, Relativistic Effects, and Adiabatic Corrections for Spectroscopic Constants of BH, CH+, and NH", J. Phys. Chem. A, p. 3068, vol. 108, (2004). Published

Mutasem Omar Sinnokrot and C. David Sherrill, "Substituent Effects in Pi-Pi Interactions: Sandwich and T-shaped Configurations", J. Am. Chem. Soc., p. 7690, vol. 126, (2004). Published

Arteum D. Bochevarov and C. David Sherrill, "A General Diagrammatic Algorithm for Contraction and Subsequent Simplification of Second-Quantized Expressions", J. Chem. Phys., p. 3374, vol. 121, (2004). Published

Micah L. Abrams and C. David Sherrill, "Natural Orbitals as Substitutes for Optimized Orbitals in Complete Active Space Wavefunctions", Chem. Phys. Lett., p. 227, vol. 395, (2004). Published

Micah L. Abrams and C. David Sherrill, "Full Configuration Interaction Potential Energy Curves for the X 1Sigmag+, B 1Deltag, and B' 1Sigmag+ States of C2: A Challenge for Approximate Methods", J. Chem. Phys., p. 9211, vol. 121, (2004). Published

Mutasem Omar Sinnokrot and C. David Sherrill, "Accurate Coupled Cluster Potential Energy Curves for Benzene Dimer: The Sandwich, T-Shaped, and Parallel-Displaced Configurations", J. Phys. Chem. A, p. 10200, vol. 108, (2004). Published

Tony P. Tauer, M. Elizabeth Derrick, and C. David Sherrill, "Estimates of the Ab Initio Limit for Sulfur-Pi Interactions: The H2S-Benzene Dimer", J. Phys. Chem. A, p. 191, vol. 109, (2005). Published

John S. Sears and C. David Sherrill, "On the Choice of Reference in Multi-Reference Electronic Structure Theory: Minimal References for Bond Breaking", Mol. Phys., p. 803, vol. 103, (2005). Published

Berhane Temelso and C. David Sherrill, "High Accuracy ab initio Studies of Li6+, Li6-, and Three Isomers of Li6", J. Chem. Phys., p. 064315, vol. 122, (2005). Published

C. D. Sherrill and P. Piecuch, "The X 1Sigmag+, B 1Deltag, and B' 1Sigmag+ States of C2: A Comparison of Renormalized Coupled-Cluster and Multireference Methods with Full Configuration Interaction Benchmarks", J. Chem. Phys., p. 124104, vol. 122, (2005). Published

Micah L. Abrams and C. David Sherrill, "General-Order Single- and Multi-Reference Configuration Interaction and Coupled-Cluster Theory: Symmetric Dissociation of Water", Chem. Phys. Lett., p. 284, vol. 404, (2005). Published

A. D. Bochevarov and C. D. Sherrill, "Hybrid Correlation Models Based on Active-Space Partitioning: Correcting Second-order Moeller-Plesset Perturbation Theory for Bond-Breaking Reactions", J. Chem. Phys., p. 234110, vol. 122, (2005). Published

M. L. Abrams and C. D. Sherrill, "Important Configurations in Configuration Interaction and Coupled-Cluster Wave Functions", Chem. Phys. Lett., p. 121, vol. 412, (2005). Published

T. P. Tauer and C. D. Sherrill, "Beyond the Benzene Dimer: An Investigation of the Additivity of Pi-Pi Interactions", J. Chem. Phys. A, p. 10475, vol. 109, (2005). Published

M. L. Abrams and C. D. Sherrill, "On the Orbital Dependence of Compact, Weight-Selected Configuration Interaction and Coupled-Cluster Wave Functions", Mol. Phys., p. 3315, vol. 103, (2005). Published

A. L. Ringer, M. O. Sinnokrot, R. P. Lively, and C. D. Sherrill, "The Effect of Multiple Substituents on Sandwith and T-Shaped Pi-Pi Interactions", Chem. Eur. J., p. 3821, vol. 12, (2006). Published

A. D. Bochevarov and C. D. Sherrill, "Some Simple Results following from Lowdin's Partitioning Technique", J. Math. Chem., p. 59, vol. 42, (2007). Published

J. S. Sears and C. D. Sherrill, "The electronic structure of oxo-Mn(salen): Single-reference and multireference approaches", J. Chem. Phys., p. 144314, vol. 124, (2006). Published

Arteum D. Bochevarov, Berhane Temelso, and C. David Sherrill, "Hybrid Correlation Models Based on Active-Space Partitioning: Seeking Accurate O(N5) Ab Initio Methods for Bond Breaking", J. Chem. Phys., p. 054109, vol. 125, (2006). Published

Mutasem Omar Sinnokrot and C. David Sherrill, "High-Accuracy Quantum Mechanical Studies of Pi-Pi Interactions in Benzene Dimers", J. Phys. Chem. A, p. 10656, vol. 110, (2006). Published

Ashley L. Ringer, Michelle S. Figgs, Mutasem Omar Sinnokrot, and C. David Sherrill, "Aliphatic C-H/Pi Interactions: Methane-Benzene, Methane-Phenol, and Methane-Indole Complexes", J. Phys. Chem. A, p. 10822, vol. 110, (2006). Published

Berhane Temelso, C. David Sherrill, Ralph C. Merkle, and Robert A. Freitas, "High-Level Ab Initio Studies of Hydrogen Abstraction From Prototype Hydrocarbon Systems", J. Phys. Chem. A, p. 10822, vol. 110, (2006). Published

T. Daniel Crawford, C. David Sherrill, Edward F. Valeev, Justin T. Fermann, Rollin A. King, Matthew L. Leininger, Shawn T. Brown, Curtis L. Janssen, Edward T. Seidl, Joseph P. Kenny, and Wesley D. Allen, "PSI3: An Open-Source Ab Initio Electronic Structure Package", J. Comput. Chem., p. 1610, vol. 28, (2007). Published

Books or Other One-time Publications

C. David Sherrill, Antara Dutta, Micah L. Abrams, and John S. Sears, "Bond Breaking in Quantum Chemistry: A Comparison of Single- and Multi-Reference Methods", ( ). Book, Submitted
Editor(s): Angela Wilson
Collection: Recent Advances in Electron Correlation Methodology
Bibliography: ACS Symposium Series

Web/Internet Site

URL(s):
http://vergil.chemistry.gatech.edu/research/bondbreaking/index.html
Description:
This webpage summarizes some of our work on bond-breaking.

Other Specific Products

Product Type:
Software (or netware)
Product Description:
We have developed a new quantum chemistry package, PSI3, which performs Hartree-Fock, complete-active-space self-consistent-field, perturbation theory, coupled-cluster, and configuration interaction computations. The program has some unique capabilities, such as a very fast full CI code and a shared-memory parallel MP2-R12 program.
Sharing Information:
The code is freely available, under the Gnu general public license, at our website, http://www.psicode.org.

Contributions

Contributions within Discipline:
Quantum mechanical models of chemical systems are having an increasing impact on chemistry, biology, materials science, engineering, and other disciplines because they can provide reliable predictions of molecular shapes and properties in many cases. Rapid improvements in

computer hardware and improved theoretical techniques are making these models easier to apply to larger molecules. However, there remain many unsolved problems in quantum chemistry, where no reliable methods yet exist, or the available models are prohibitively expensive computationally. Our research focuses on the development and application of new theoretical models to challenging chemical problems, particularly for the reliable description of potential energy surfaces.

We have developed a large program package, PSI3, which will assist in the development and application of electronic structure theory to interesting chemical problems. This open-source program is distributed over the internet for free.

Potential energy surfaces for weakly bound systems are challenging to compute because dispersion interactions are hard to model without very large basis sets, and high levels of correlation also appear to be important. However, noncovalent interactions are of central importance in understanding molecular recognition, supramolecular assembly, and crystal packing in many materials. Advances in rational drug design will depend on a better understanding of noncovalent interactions. We have obtained the first reliable description of the simplest prototype of pi-pi interactions, the benzene dimer, by developing new explicitly correlated (R12) methods for parallel computers. We find that the perpendicular and parallel-displaced configurations are both bound by just under 3 kcal/mol, a number significantly larger than the experimental estimate. Our results also shed light on the fundamental nature and geometric dependence of this pi-pi interaction. We also presented the first high-level theoretical studies of substituent effects in these systems and showed that dispersion, not electrostatics, is the dominant term in total binding energies. We have shown that the reigning paradigm in understanding substituent effects in pi-pi interactions, the Hunter-Sanders rules, give the wrong answers for monosubstituted or multi-substituted benzene heterodimers. Those rules rely solely on electrostatics and neglect important changes in relative dispersion energies which we elucidate. Our conclusions immediately impact the qualitative understanding of substituent effects in pi-pi interactions, a subject of interest in rational drug design.

Our first-ever, benchmark-quality studies of potential energy curves in benzene dimer, H2S-benzene, and methane-benzene, methane-phenol, and methane-indole have shown how the noncovalent interactions in these systems depend on geometry and distance. They elucidate the nature of pi-pi, sulfur-pi, and CH/pi interactions, and they are proving invaluable in the calibration and benchmarking of new, approximate methods to accurately model these interactions in the context of large biomolecular simulations. The groups of MacKerell, Friesner, Berne, Roethlisberger, Grimme, Schutz, Jansen, Truhlar, and others have already calibrated their new force-field or improved DFT methods against our published data.

We resolved the controversy over the structure of Li6, a cluster with many structures which have similar stabilities. Our work sheds light on how geometries of small clusters transition from 2D to 3D as the size of the cluster grows.

We have extended the theoretical understanding of bond breaking reactions by providing the most complete benchmark potential energy curves published to date for several small molecules. These benchmarks will be useful to theorists who are developing new bond breaking models. We have also used these benchmarks to calibrate standard theoretical approaches to see how well they perform for bond breaking. Even very elaborate and usually reliable methods like CCSD(T) exhibit large (~3 kcal/mol) errors for 'easy' bond-breaking reactions, and much worse errors (~20 kcal/mol) for 'difficult' ones. Multi-reference methods, which are designed to handle bond breaking reactions, are generally much more reliable but can also exhibit large errors if the space of active orbitals is not appropriately chosen. Our results are among the first to systematically show how different choices of active space affect the accuracy of the results across an entire potential energy curve.

In addition, we have presented some new techniques for the theoretical description of bond-breaking reactions, diradicals, and other nondynamical correlation problems. We have presented a new way to solve for orbitals in difficult multiconfigurational self-consistent-field (MCSCF) computations. We have also extended the ``spin-flip" CIS method to include dynamic correlation perturbatively and shown that this can lead to reliable predictions for several systems. This adds to the body of knowledge in dealing with these tricky electronic structure problems. We have also solved a problem with the original spin-flip approach which reduces errors substantially.

Using new a new program capable of handling electronic excitations through arbitrary orders, we have shown that in bond-breaking reactions only a few of the higher-order electron correlation terms are actually important, and that very compact CI or coupled-cluster wavefunctions, using only ~2% of the wavefunction, can still achieve very high accuracies (nonparallelity errors of less than 1 kcal/mol). The general-order coupled-cluster wavefunctions are found to be less sensitive to the choice of orbitals than the corresponding CI wavefunctions, although of course the sensitivity decreases with increasing completeness of the CI/CC treatment.

We have discovered very effective ways to improve second-order perturbation theory (MP2) for bond-breaking reactions and also for equilibrium molecular properties based on correspondences between MP2 and CCSD theory. Certain terms can be replaced with their CCSD counterparts at only marginally increased cost, yielding an MP2-CCSD hybrid method of great promise for situations, like bond-breaking, where MP2 fails totally. This approach should also be helpful in a MP2-CCSD(T) form which can give accurate results for pi-pi and noncovalent interactions at greatly reduced computational cost.

We are the first to have tested certain types of orbitals for use in bond-breaking theories. We demonstrated that ``natural orbitals" from electron correlation theories can provide an inexpensive alternative to CASSCF orbitals. We also were the first to show how unrestricted orbitals work in multireference coupled-cluster theory. These studies will help theorists better understand how to handle bond-breaking reactions.

In the course of our more formal theoretical work, we have developed programs which assist in automating the derivation of equations for complex electron correlation theories (Nostromo program) using diagrammatic techniques, and in the implementation of arbitrarily complex methods (DBQC toolkit). These programs will help us and others create and test new theoretical methods more easily.

We have demonstrated that the Born-Oppenheimer diagonal correction (BODC), which is required for attaining spectroscopic accuracy, is relatively well approximated at the Hartree-Fock level of theory, but requires more elaborate theoretical treatment to achieve with very high accuracy. This impacts theoretical predictions of very highly vibrationally excited levels; this relates, for example, to the recent controversy over whether water exists on the sun. Compared to more commonly employed small corrections such as basis set extrapolation and relativistic effects, the BODC can be even more important in determining molecular properties of hydrides such as BH, CH+, and NH.

Many radicals containing at least two symmetry-equivalent atoms are a particularly vexing challenge for theoretical modeling, because they often exhibit a phenomenon called ``artifactual symmetry breaking," which means that the radical electron localizes on one atom or the other instead of staying properly delocalized. When this occurs, predictions of molecular properties can be totally ruined (e.g., unphysically large vibrational frequencies can result). This problem has been observed for some diradicals also. We have performed the most complete comparison to date of the molecular property predictions of different theoretical methods for a series of symmetry breaking molecules. We found that density functional theory (DFT) is among the more reliable methods for these systems, but there are still examples where it fails. We also showed that none of the currently proposed explanations for the anomalous property predictions in these molecules is sufficient to account for all of our observations.

Contributions to Other Disciplines:

Our open-source program package, PSI3, is freely available and is expected to assist researchers in other disciplines to use computational chemistry techniques in their research. Quantum mechanical results from PSI3 may inform larger-scale studies of materials or biomolecules.

Our results on weak interactions are being used to parameterize new force-field or DFT methods for large-scale simulations, particularly of biomolecules. These simulations, in turn, will assist in rational drug design and ultimately in the development of improved pharmaceuticals. Our results on substituent effects in pi-pi interactions overturn the conventional wisdom on this subject and will also assist drug design efforts, as many drugs use pi-pi interactions in their binding (including, for example, intercalating anti-cancer agents or the anti-Alzheimer's drug Aricept).

Contributions to Human Resource Development:

So far, this project has contributed to the training of nine graduate students, two postdocs, and four undergraduate students. Educational materials developed under this project have found a variety of uses, including an NSF-sponsored Workshop in Theoretical and Computational Chemistry for faculty at small colleges.

Contributions to Resources for Research and Education:

One of the computers purchased for this project is being used, among other roles, as a web server to help disseminate our results to the public.

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Contributions: To Any Beyond Science and Engineering

Project Activities, Cumulative

Goals

Our primary goal is to extend the reach of quantum chemistry methods to difficult cases. This project focuses on systems where electron correlation effects can be critical, either in those systems where more than one electron configuration is important (i.e., nondynamical electron correlation, such as bond-breaking reactions and diradicals), or in weakly-bound systems where qualitatively incorrect solutions are obtained unless robust models of dynamical correlation are employed.

We have pursued a dual-track strategy of (a) developing new theoretical methods and implementing them as efficient computer programs, and (b) applying new and existing methods to key prototype chemical systems which are challenging to model.

Our work has been presented at departmental seminars across the US and at numerous national and international conferences. In addition to journal publications, an invited book chapter on bond-breaking was contributed to the inaugural issue of *Annual Reports in Computational Chemistry*.

Activities

Electronic structure programs

Much of our work involves theoretical development and computer programming. Believing that theoretical and computational chemistry research in the US will benefit tremendously from the widespread, free availability of tools for the development and application of electronic structure methods, we have embarked upon a project to make as many of these tools available as possible through our open-source program package, PSI3, developed in collaboration with Prof. Daniel Crawford (Virginia Tech). Our code was publicly released for the first time in 2003, and it is freely available on our website `http://www.psicode.org`. The program has CI, MP2, CCSD, CCSD(T), CASSCF, MRCI, MP2-R12/A, and other capabilities. Over the past few years, we have run multiple-day PSI3 programming workshops with other theory groups to extend the impact of this program.

We significantly expanded the CI components of the PSI3 program during the course of this project, adding arbitrary-order coupled-cluster theory including active spaces; a "spin-complete" version of Krylov's spin-flip method; CI density and transition density matrices, and various MCSCF-related methods including line-minimization techniques for orbital optimization (with Mark Hoffmann), restricted active space self-consistent-field (RASSCF), and various approximate orbital Hessians. We developed other programs to perform MP2-CCSD "hybrid" computations, to perform coupled electron/nuclear

molecular orbital computations, and to perform computer-automated derivation of complicated many-body theories.

Potential energy surfaces of strongly interacting systems and nondynamical correlation

During the course of the project, we published several key studies of potential energy curves for bond-breaking reactions where we obtained the *exact* numerical solution of the electronic Schrödinger equation (within the space spanned by the given one-particle basis set) using our state-of-the-art full configuration interaction program, DETCI. These exact potential energy curves are invaluable in benchmarking approximate methods for bond-breaking reactions and other cases of electronic near-degeneracies. We benchmarked several common single-reference theories [MP2, CISD, CCSD, CCSD(T)] with RHF and UHF orbitals, and we found surprisingly large errors for the simple reactions removing a hydrogen from BH, CH_4, and HF. We also examined the very interesting C_2 molecule, which features unusual bonding (two π bonds and no σ bond) and very low-lying electronic excited states. The results from this study were so intriguing that they inspired a subsequent study, in collaboration with Piotr Piecuch, in which multi-reference methods (CASPT2 and MRCI) are pitted against Piecuch's completely-renormalized coupled-cluster methods for this challenging test case.

Although multi-reference methods can provide accurate results for bond-breaking reactions, they are harder to use for the non-specialist because they require the specification of an active space. We have performed what we believe is the first systematic study on the proper choice of active spaces for such problems. Comparing against our own full CI data and that of Olsen, we have evaluated various *a priori* choices of active spaces for use in CASPT2 and MRCI computations: a valence active space, a "one-to-one" active space, and (recently) minimal choices of active space (e.g., 2 electrons in 2 orbitals for a single bond broken). We believe that our two publications on this topic (with student John Sears) will ultimately help establish the "best" methodology for choosing active spaces, if such a thing exists, and at the very least our data will provide desparately-needed guidance for non-experts.

We implemented code to obtain natural orbitals for configuration interaction (CI), second-order perturbation theory (MP2), and coupled-cluster theory (CCSD), and we published a study of how these natural orbitals can be used as substitutes for the usual CASSCF orbitals in complete-active-space second-order perturbation theory (CASPT2) or multi-reference configuration interaction (MRCI) computations.

Student Micah Abrams implemented a pilot code DBQC, which uses determinant and string techniques for rapidly implementing arbitrary-order configuration interaction, perturbation theory, or coupled-cluster theory calculations. The program can compute coupled-cluster energies using single, double, triple, quadruple, and pentuple excitations (CCSDTQP), or any higher excitation level desired. Multi-reference CI and perturbation theory, and also state-selective multi-reference coupled-cluster theories were also implemented. Both restricted and unrestricted orbitals may be used. This code is allowing us to better

understand the electron correlation problem in bond-breaking reactions. Micah presented this work in a talk at the 2004 meeting of the Southeast Theoretical Chemistry Association, where he won the award for best student lecture. He also won 1st place for this work in our department's annual House-Flaschka-Ashby graduate research symposium (October, 2004). Results obtained from these preliminary studies (presented in 3 publications) were helpful as we developed a more robust, production-level program.

We then adapted our very efficient DETCI program to perform these arbitrary-order coupled-cluster computations. The DETCI-based code proved vastly superior to the initial pilot code because of its very fast computation of the product of the Hamiltonian with a trial vector. This new code is being used to begin exploring how higher-order excitations in coupled-cluster theory might be most effectively included. We believe, based on our initial results, that only a few of the higher-order terms are actually important, and we are exploring how they may be included inexpensively. Preliminary results for spectroscopic constants and bond-breaking curves of small molecules have been obtained with this code supporting our hypothesis.

In other attempts to obtain high-quality results at a lower compuational cost, we developed a hybrid theory which combines the (relatively) inexpensive cost of MP2 with the more reliable results of CCSD. To do this we exploited the theoretical connections between these two methods. In two publications, various flavors of such methods are proposed, implemented, and tested. Such methods will be very valuable not only in cases of mild near-degeneracies, but also in noncovalent interactions (below). Student Arteum Bochevarov presented this work at the National ACS meeting in Washington, D. C. (Fall 2005), and two publications have resulted from this work. We found that the hybrid MP2-CCSD also improves upon MP2 significantly for equilibrium properties.

Student Berhane Temelso studied bond-breaking reactions in various hydrogen transfer reactions between organics. This topic is important for many different applications. This work resulted in two appliations papers which also contained full CI benchmarks for the smaller systems. We believe these systems might prove fruitful for testing the MP2-CCSD hybrids described above, because traditional MP2 had difficulties.

Student Arteum Bochevarov explored how computers can assist in the tedious derivation of higher-order correlation theories. Instead of using Wick's theorem, as has been done by a few others in the past, Arteum has explored using diagrams directly. The simplification of the final expressions requires the detection of equivalent diagrams, and Arteum is able to perform this efficiently (in polynomial, rather than factorial time) via topological analysis of the diagrams in most cases. A program, *Nostromo*, was developed to perform these manipulations, and it has been described in *J. Chem. Phys.* in 2004. Arteum also presented this work in a talk at the 2004 meeting of the Southeast Theoretical Chemistry Association and at the conference "Molecular Quantum Mechanics" honoring Prof. Nicholas Handy at Cambridge University in July 2004. Other purely mathematical work by Arteum resulted in a paper on Løwdin's partitioning technique in *J. Math. Chem.*

Potential energy surfaces of weakly interacting systems and molecular recognition

Potential energy surfaces of weakly interacting systems are also challenging. As in bond breaking reactions, higher-order electron correlations can be important in achieving high accuracy. Additionally, very large basis sets are required.

Following up on our definitive 2002 study of the simplest prototype of aromatic π-π interactions, the benzene dimer, we began obtaining high-quality energies for entire potential energy curves, and not just the equilibrium geometries. This work was completed and published in 2004. Preliminary data was sent to our collaborators Prof. Alex MacKerell (University of Maryland) and Prof. Ian Gould (Imperial College, London) to assist their development and testing of force fields for biomolecules.

In 2004, we completed a study (published in JACS) which explored how π-π interactions can be tuned by substituent effects. This fundamental question in molecular recognition and self-assembly had not yet been seriously addressed. We performed computations on various substituted benzene dimers to discover changes in binding energy as a function of substitution, and we analyzed the results using symmetry-adapted perturbation theory to elucidate the importance of dispersion vs. electrostatics. In 2006, we published a paper (*Chem. Eur. J.*) exploring the effect of *multiple* substituents. The goal here is to provide a simple picture of how substituents can be used to adjust π-π interactions, and student Ashley Ringer developed a simple equation (based on, for example, Hammett parameters and polarizabilities) which might predict the energy change in π-π interactions due to substituents. Even qualitative or semi-quantitative rules would assist efforts in rational drug design because many drugs, including anti-cancer intercalating drugs and the anti-Alzheimers drug Aricept, use π-π interactions in their binding.

To understand how π-π interactions act in clusters (e.g., stacks of aromatic molecules as used in some "molecular wires," or the interaction of three or four armoatic side-chains in proteins such as cold-shock protein A), we published a study (2005) of benzene trimers and tetramers. The goal of this work was to understand whether the π-π interactions are *additive or not additive*; i.e., if a third phenylalanine is brought close to a pair of phenylalanines, do polarization effects cause the trimer interaction energy to be more than, less than, or about the same as what would be found for the interactions between isolated pairs? This was the 2nd most accessed article in *J. Phys. Chem. A* for 4th quarter, 2005.

Our work on substituted benzene dimers has been summarized in a Feature Article of *J. Phys. Chem. A* (September, 2007).

In a first step at understanding charge transport in organic materials, we have also studied the benzene dimer cation. These studies are very difficult because of the possible influence of artifactual symmetry breaking, another topic of interest to us in this project. We published a study comparing a number of theoretical methods for well-known symmetry breaking problems and discovered that a well-known IR assignment for the atmospherically important molecule O_4^+ may be incorrect.

In an examination of another noncovalent interaction important to biochemistry, student Tony Tauer and NSF Faculty Development Program Visiting Professor Elizabeth Derrick (Valdosta State University)

performed computations of sulfur-π interactions. We began with the simplest prototype, benzene-H_2S, to understand basis set and electron correlation effects. The geometric dependence of the interaction energy and its decomposition into electrostatic, dispersion, indiction, and exchange-repulsion components was analyzed, similar to our studies of benzene dimer.

NSF graduate fellow Ashley Ringer published a study on CH/π interactions as seen in the prototype system methane-benzene. This work provided benchmark-quality potential curves and also demonstrated that some features of the prototype complex (minimum interfragment distance) are also those seen in the protein databank for CH/π interactions.

Other work on noncovalent interactions was pursued by NSF REU students Michelle Szeto, Hugh Heldenbrand, and Ryan Steele. We performed high-quality computations on the potential energy surfaces of methane interacting with various aromatic sidechains of amino acids to better understand alkyl-π interactions, and similar computations on benzene-cation complexes to better understand cation-π interactions.

In work intermediate between our two areas of strongly and weakly interacting systems, student Berhane Temelso studied Li_6, where the intermediate bonding strength leads to clusters in which the structures are much less fluxional than in the nonbonding interactions, but there are several energetically competitive minima. We used high-level methods [CCSD(T)/cc-pCVQZ] to obtain definitive results for the structures and spectroscopic properties of various Li_6 isomers, for which 2D and 3D structures are competitive energetically.

Other challenging systems

During the course of the project, we also performed a systematic study to compare the various small sources of error in electronic structure computations. We published a paper on the effect of one-particle basis set completeness, higher-order electron correlation, relativistic effects, and adiabatic corrections for spectroscopic constants of BH, CH^+, and NH. We examined the accuracy limits of orbital expansion methods by looking at k orbitals. We explored computations of the Born-Oppenheimer correction using electron correlation methods. We presented high-quality data for the ethylene radical cation to resolve some experimental questions about its structure and spectrum.

Educational activities

Throughout the duration of the grant, the PI participated as an instructor of the NSF Workshop on Computational and Theoretical Chemistry. To date, more than 60 faculty from small colleges have participated in this program to learn how to use computational chemistry in lab modules and in research with undergraduates. Many of the participants taught in areas other than physical chemistry. The week long

course (co-taught with Rigoberto Hernandez) featured morning lectures and afternoon computer labs. Topics included a review of classical and quantum mechanics, Hartree-Fock theory, basis sets, geometry optimization, electron correlation, molecular vibrations, and computing thermodynamic properties.

The PI has established an annual Summer Theory Program at Georgia Tech for undergraduate researchers and beginning graduate students. The program involves introductory lectures in theoretical chemistry in addition to summer research. Approximately ten NSF REU students at Georgia Tech have gone through the program.

The PI has also developed a very popular set of online lecture notes in quantum chemistry which have been used as a supplement to the NSF Workshop on Computational and Theoretical Chemistry and for the Summer Theory Program. These notes are also widely accessed internationally by students from high-school through graduate school.

Project Findings, Cumulative

Potential energy landscapes of strongly interacting systems and nondynamical correlation

We have implemented a prototype code which can generate single- and state-selective multi-reference coupled-cluster theories at any order (e.g., CCSD, CCSDT, CCSDTQ, ...). In the first study of its kind (*Chem. Phys. Lett.*, 2005), we discovered that, contrary to conventional wisdom, UHF references do *not* necessarily improve the quality of the potentials for these single- and multi-reference coupled-cluster theories. We also used this code to make the remarkable discovery (*Chem. Phys. Lett.*, 2005) that very compact coupled-cluster wavefunctions (2% of full expansion) can, in principle, be constructed for accurately describing potential energy surfaces (errors less than 1 kcal mol^{-1}); these expansions require the limited inclusion of higher-order excitations (up to connected pentuples for double bond breaking in H_2O), and the next step will be to create an algorithm to select the most important configurations efficiently. The orbital dependence of CI and CC methods which select excitations based on the size of their coefficients has also been explored (*Mol. Phys.*, 2005) Based on these encouraging results, a new, production-level arbitrary-order coupled-cluster code has been implemented based on our efficient DETCI program. New test cases and various configuration selection schemes are being tested with the new code. Initial results strongly suggest that the Hoffmann's macroconfiguration concept can be very effective at selecting the few higher-order electron configurations necessary in coupled-cluster applications where high accuracy is required or where chemical bonds are broken.

To make it easier to implement and test new theoretical methods, we have developed a toolkit (DBQC) which uses techniques from determinant-based CI. We find so far that this approach is a fruitful one, as it formed the basis of the arbitrary-order coupled-cluster work described above. To more easily derive the complex equations for complicated many-body methods, we have created a program called *Nostromo* which automates the generation and analysis of many-body diagrams (*J. Chem. Phys.*, 2004). We find that a purely-diagrammatic approach has some advantages over methods relying on Wick's theorem, and compared to tools like Hirata's tensor contraction engine, we can usually determine diagram equivalence in *polynomial* as opposed to *factorial* time. The algorithm is fast and its implementation is user-friendly. For example, it takes just minutes to generate the simplified programmable expression for a CCSDTQ matrix element.

In an attempt to lower the cost of CASSCF computations in cases where very large active spaces might be required, we discovered (*Chem. Phys. Lett.*, 2004) that natural orbitals from correlated, single-reference wavefunctions provide excellent approximations to CASSCF orbitals for reactions breaking single or even double bonds. CCSD natural orbitals, in particular, are of very high quality and provide excellent guesses to (or even replacements for) CASSCF orbitals. If a CASSCF procedure takes 10 iterations, then replacing the CASSCF orbitals by these natural orbitals would reduce the cost of the active-space CI calculation by this same factor of 10 (the cost of obtaining the natural orbitals vanishes relative to the

active-space CI calculation for large active spaces).

Our full CI studies of the $\tilde{X}\ ^1\Sigma_g^+$, $\tilde{B}\ ^1\Delta_g$, and $\tilde{B}'\ ^1\Sigma_g^+$ states of C_2 (*J. Chem. Phys.*, 2004) showed that no standard single-reference method is able to come close to reproducing the shapes of the potential energy curves for any of these three states. The potential curve of the ground state is very non-Morse-like because of an avoided crossing with the $\tilde{B}'\ ^1\Sigma_g^+$ state at intermediate distances, and none of the standard single-reference methods capture this effect. The excited states are difficult for standard single-reference methods because they look like doubly excited states relative to the dominant ground-state Hartree-Fock determinant. Apart from a study of ionic/covalent curves in LiF by Bauschlicher, we believe this is the only available full CI study of avoided crossings, and it is the only rigorous assessment of coupled-cluster methods in such situations. This work is also one of the only detailed full CI studies of excited state potentials ever published. Our work provides a critical new benchmark for the assessment of theoretical methods for bond-breaking reactions. It has already led to one collaboration with Piecuch comparing his completely-renormalized coupled-cluster method against multi-reference methods produced by us (*J. Chem. Phys.*, 2005), where we find that completely-renormalized coupled-cluster works roughly as well as CASPT2 so long as the bond is not stretched much beyond 2.0 Å. Our studies have motivated a number of other theoretical papers which examine various methods as compared to our benchmark data.

In two studies on the choice of active spaces (*J. Phys. Chem. A*, 2003; *Mol. Phys.*, 2005) we found that minimal active spaces performed about as well as valence active spaces or one-to-one active spaces for bond-breaking reactions in HF, BH, CH_4, H_2O, and N_2 when CASPT2 or multi-reference CI methods are used. Moreover, a product of 2x2 active spaces was found effective in limited tests for breaking multiple bonds in H_2O and N_2. We also discovered a surprise in our analysis of CASSCF using different active spaces for HF: for the valence active space, apparently there is an (unphysical) mixing between the F core orbital and F lone-pair valence orbitals with occupation numbers near two (such a mixing would hardly change the CASSCF energy, thus it could be allowed). This may be a more general problem which can plague CASSCF computations for some choices of active spaces.

Our study on DFT and symmetry breaking (*J. Chem. Phys.*, 2001) is the most complete comparison to date of the performance of electronic structure methods in predicting molecular properties of molecules prone to artifactual spatial symmetry breaking. We considered the symmetry breaking molecules NO_3, O_4^+, F_4^+, F_2^+, and O_2^+ and applied a wide variety of methods [Hartree-Fock, MP2, S-VWN, BLYP, B3LYP, BPW91, and B3PW91, CCSD, CCSD(T), Brueckner CCD, Brueckner CCD(T)] with three different basis sets to compute equilibrium geometries and harmonic vibrational frequencies.

In collaboration with Prof. Anna Krylov (USC), we have adapted our group's CI code to mimic Krylov's spin-flip CIS method (*J. Chem. Phys.*, 2003). We corrected a deficiency in the original approach, which is that the theory generated spin-contaminated wavefunctions. Our new approach, which we have named "spin-complete" spin-flip CIS (SC-SF-CIS) reduces errors in the basic SF-CIS by as much as 1/2 to 2/3 without increasing the OV scaling of the method. Perturbative corrections for dynamic correlation, analogous to the SF-CIS(D) method reported last year, could yield a bond breaking model which is relatively inexpensive yet quantitatively reliable across entire potential energy surfaces.

For the first time, we have investigated both the basis set and correlation convergence of the so-called Born-Oppenheimer diagonal correction (BODC), which is a small correction on the order of 10-100 cm^{-1} (*J. Chem. Phys.*, 2003). We have found that convergence with respect to correlation treatment is fairly rapid, and even Hartree-Fock estimates are fairly reliable. Basis set convergence is not quite as fast, but triple-zeta basis sets give only small errors. However, it is quite difficult to obtain the BODC very accurately, as is required for spectroscopic accuracy of the type needed to model high vibrational levels of polyatomic molecules like H_2O.

Based on our work on the Born-Oppenheimer diagonal correction (BODC), we assessed its importance to the spectroscopic constants of BH, CH^+, and NH, for which we could compute near-exact results including basis set extrapolations, corrections for excitations beyond those in CCSD(T), and relativistic corrections. Our paper (*J. Phys. Chem. A*, 2004) shows that nonadiabatic effects can be surprisingly large in these diatomic hydrides, and for BH and CH^+, they are the *largest* effect among those considered when trying to correct the bond length beyond the CCSD(T)/cc-pCV5Z level of theory. For the bond lengths and vibrational frequencies of the three molecules considered, the BODC correction is at least as important as basis set extrapolation. With the exception of negligible contributions to the bond length due to relativity, all of the small effects considered are of roughly equal importance, demonstrating the difficulty of computing molecular properties to spectroscopic accuracy. On the other hand, when all these contributions are included, bond lengths match experiment within 0.0007 Å, and harmonic frequencies are within 0.5 cm^{-1} of experiment.

We have investigated various "simple" methods to solve for electron and nuclear motions simultaneously. In an approach we call electronic and nuclear molecular orbitals (ENMO), the wavefunction is written as a direct product of Slater determinants, each of them pertaining to a different kind of particles that make up the molecule, i.e., electrons and nuclei (*Mol. Phys.*, 2004). We are investigating the ability of ENMO to describe the non-adiabatic effects in light atoms and molecules. Both Many-Body Perturbation Theory (MBPT) and Configuration Interaction for Singles and Doubles (CISD) extensions of the mean-field ENMO are being applied to study the correlation effects. So far, we have found that the adequate separation of the center-of-mass motion is pivotal for the accuracy of results. The electronic-nuclear contribution to the correlation energy has been found to be sizeable. Moreover, our results suggest that the main source of error in an approach like this is the non-factorizability of the trial wavefunction into center-of-mass and internal components. This work has been of great utility to other groups pushing to use these kinds of methods for hydrogen transfer reactions and other applications, as it has influenced the course of their methods development.

Our work on hybrid MP2-CCSD methods (*J. Chem. Phys.*, 2005-6) showed us that it is indeed possible to obtain near-CCSD-quality results using a method which is largely at the cost of the less expensive MP2. In two publications we show the theory and performance of this hybrid methodology. After analyzing the failures of MP2 for bond-breaking reactions, we select certain wavefunction amplitudes to treat at the more robust CCSD level of theory. The hybrid MP2-CCSD method is able to break single bonds qualitatively correctly, instead of providing diverging energies like MP2 does when using restricted

orbitals. Molecular properties are also greatly improved over simple MP2 in our hybrid methodology, but with the same computational scaling as MP2. We are very enthusiastic about the application of such methods for more reliable computations of transition states and for much more accurate interaction energies for large, weakly bound systems (below) at the cost of MP2.

Potential energy landscapes of weakly interacting systems and molecular recognition

In very highly cited work (*J. Am. Chem. Soc.*, 2002), we made significant contributions to the understanding of π-π interactions in molecular recognition and supramolecular chemistry by performing the first definitive work on the prototype π-π system, the benzene dimer. Our results for the first time reveal basis set effects and provide estimates of the *ab initio* limit for the binding energies of three dimer configurations, the parallel stacked sandwich, the perpendicular T-shape, and the offset parallel displaced geometries. Our explicitly correlated MP2-R12/A results should be very close to the complete basis set MP2 limits. When corrected for higher-level correlation via CCSD(T), our binding energies should be accurate to a few tenths of a kcal mol^{-1}. In agreement with lower-level computations, we find that the T-shape and parallel displaced configurations are the most stable of those considered, and are nearly isoenergetic. However, our final binding energies (just under 3 kcal mol^{-1}) are significantly larger than in previous work and definitively refute the experimental value of 1.6 ± 0.2 kcal mol^{-1}. This work proved to be a launching-point for extensive additional work in this area.

We demonstrated (*J. Phys. Chem. A*, 2003; *J. Am. Chem. Soc.*, 2004) that the prevailing model used by biochemists to understand substituent effects in π-π interactions, the Hunter-Sanders model, gives wrong predictions for the simplest model system, substituted benzene dimers. The Hunter-Sanders model argues that although dispersion is important to the attraction between π systems, it is mostly nondirectional, and geometries and substituent effects are governed instead by electrostatic interactions. For strongly electron withdrawing groups such as F and CN, this is true. For weak electron donors such as CH_3, it is false; changes to the dispersion interaction dominate the substituent effect. Our paper has created significant interest among those working in molecular recognition and it has implications for rational drug design. Extension of this work to *multiple* substituents indicates that *the substituent effects are additive*, at least in certain configurations, and this is a tremendously promising finding in that it makes these effects much easier to understand. We have developed a simple model, based on properties like polarizabilities and Hammett parameters, which appears to provide good estimates of how much a π-π interaction is tuned by substituents for sandwich and T-shaped configurations (*Chem. Eur. J.*, 2006).

Our work on benzene dimer and substituted benzene dimers has been of significant interest to chemists working in supramolecular chemistry and molecular recognition, as well as to theorists. We published an invited Feature Article in *J. Phys. Chem. A* (September, 2006) summarizing our work in this area.

Work on benzene trimers and tetramers led to the very important conclusion that binding energies in

these sytems are almost completely pairwise-additive (*J. Phys. Chem. A*, 2005). Only for the cyclic trimer are there any appreciable three-body effects. This has a significant impact on the understanding of π-π interactions that occur in extended systems like molecular wires or clusters of tryptophans in proteins. It also suggests that even in organic crystals, lattice energies may be computed pairwise. We will follow up on this implication by explicit computations of crystal benzene in future work.

Other studies on the benzene dimer, benzene-H_2S, and methane-benzene, methane-phenol, and methane-indole seek to provide, for the first time, highly accurate potentials demonstrating the true geometric dependence of these interactions. Both the H_2S-benzene (*J. Phys. Chem. A*, 2005) and the methane-π studies (*J. Phys. Chem. A*, 2006) demonstrate a clear preference for the hydrogen to point toward the center of the benzene ring. Calibration studies of the theoretical methodology indicated that, consistent with our earlier work on benzene dimer, large basis sets (aug-cc-pVTZ or better) and CCSD(T) are required to achieve an accuracy of a few tenths of one kcal mol^{-1} in the binding energy. Pople-type basis sets like 6-31+G* were examined and found badly wanting for H_2S-benzene. The new study of potential curves for the benzene dimer (*J. Phys. Chem. A*, 2004) quantified the geometry-dependence of the binding energy for the T-shaped, parallel-displaced, and sandwich configurations. These potential curves also provide some of the only high-quality data available for benchmarking and/or calibrating approximate models for weak interactions. Inexpensive methods like force-field methods and density functional theory do not currently provide good results for weak interactions, and the improvement of these methods is crucial for reliable modeling of biomolecules and materials. Already several groups have published work in which they have calibrated their new methods against our benchmark-quality results: Röthlisberger, Grimme, Schütz, Langerith, Lundqvist, and Becke (various DFT dispersion models); Berne and Friesner (polarizable force field models); Grimme (spin component scaled MP2); Truhlar (multi-component DFT).

Our study of the intermediate bonding in Li_6 clusters (*J. Chem. Phys.*, 2005) definitively resolved the preferred structure by employing very high-quality methods [CCSD(T)/cc-pCVQZ] and also by comparing to the limited amount of experimental data available for properties such as electronic excitation energies. This metal hexamer is of interest because it is just large enough that 2D and 3D structures are energetically competitive. There has been significant controversy over the preferred structures of such hexamers (e.g., Au_6), but we show that for Li_6, the preferred structure is a D_{4h} distorted octahedron. This contrasts with Au_6, which apparently prefers an unusual planar, triangular shape.